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Electrochemical reduction of carbon dioxide at ruthenium dioxide deposited on boron-doped diamond

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Abstract

Study of carbon dioxide reduction at RuO_2-coated diamond electrodes showed that conductive metallic oxides are promising electrocatalysts for this process and allow higher reduction products to be obtained. The main reduction products obtained in acidic and neutral media were formic acid and methanol, with product efficiencies as high as 40 and 7.7%, respectively. It was observed that conductive diamond is a very well suited material for studying the electrocatalytic properties of conductive metallic oxides, because its use resulted in a negligible substrate effect. This feature will greatly enhance the ability to understand the relationships between the intrinsic electrochemical behavior and the electrocatalytic behavior, in view of developing new effective electrocatalysts. The use of conductive diamond could also allow better utilization of the electrocatalyst by avoiding the need for thick films.

1. Introduction

The use of carbon dioxide as a raw material for chemical syntheses is inherently a promising alternative, both from economical and ecological point of view. However, the CO_2 molecule is thermodynamically stable and, in order to efficiently convert this compound into the desired product, suitable activation mechanisms and reaction conditions have to be found. Among the various possible approaches for activating this molecule, electrochemical reduction is promising, mainly because it has the advantage that water can be used as the proton source [1]. Thus, it has been found that the direct electrochemical reduction of CO_2 results in a variety of products, the distribution of which critically depends on reaction conditions, such as electrode materials, solvent systems, and operational parameters including current density. In most of the studies made on metals with high overvoltage for hydrogen evolution, the main products of the carbon dioxide reduction were CO or formic acid [2–4]. Higher reduction products have been obtained with semiconductors [5, 6] or with some metals having medium overvoltage for hydrogen evolution [7–9].

At present, it is widely accepted that the most interesting electrode materials for CO_2 reduction are also active for hydrogen evolution. Nevertheless, the efficiency of the CO_2 conversion is affected by the fact that, due to the low solubility of carbon dioxide in water, hydrogen evolution prevails. Data from the literature are suggesting two possible approaches for improving the efficiency of the reduction process by increasing the CO_2 content in the solution: the use of aprotic solvents [10–13], and/or the use of high pressure systems [14–17]. It was also found that the selectivity for carbon dioxide reduction vs hydrogen evolution is enhanced when employing metallic catalysts on nanoporous supports [4, 18, 19].

It is noteworthy that, from a thermodynamic standpoint, the electrochemical reduction of CO_2 to higher reduction products (e.g. methanol or methane) is more favorable than water reduction [20]. Furthermore, based upon the solubility of carbon dioxide in water (*ca.* 4×10^{-2} mol l^{-1}), a value of *ca.* 0.23 A cm^{-2} can be estimated for the limiting current corresponding to the reduction of CO_2 to methanol [21]. Although this value would satisfy practical needs, the above reaction is kinetically rather complex and, if this approach is to be considered seriously, it is important to develop effective electrocatalysts. In this respect, RuO_2 is a promising material because it has high electrical conductivity and electrochemical stability, intermediate hydrogen-overvoltage and the capacity to reversibly adsorb hydrogen. Furthermore, it is relatively easy to deposit RuO_2 layers by thermal methods, and the use of this oxide as electrocatalytist is well substantiated. The use

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of RuO_2-coated titanium electrodes for CO_2 reduction was previously reported, but the results are controversial. Thus, within the pH range 4.0–7.6, Bandi [20] found the efficiency for methanol production to decrease with increase in pH. Nevertheless, for the same process, Popic et al. [22] reported high Faradaic efficiency in alkaline media. Because in both cases the electrodes were obtained by thermal methods, it seems likely to assume that these different results are due to the effect of the conditions on the titanium substrate.

In the present work we report results of the investigation of carbon dioxide reduction at the RuO_2-coated boron-doped diamond (BDD) electrodes. The excellent chemical and electrochemical stability of polycrystalline diamond [23–26] strongly commend this material as a substrate for electrocatalysts. The high overpotential that BDD exhibits both for hydrogen and oxygen evolution is also of particular interest because it allows better functioning of the catalyst with minimum substrate interference. Earlier, Duo et al. demonstrated the activation of diamond electrodes for oxygen evolution and organic oxidation, by modifying with a small amount of IrO_2 clusters [27]. Furthermore, diamond is a favorable substrate to electrochemically deposit metal or metal oxide clusters discontinuously, due its inhomogeneity of nucleation sites [28, N. Spataru et al. and C. Tershima et al., submitted for publication]. This allows the deposition of discontinuous films of RuO_2, thus maximizing the utilization of the catalyst for CO_2 reduction by avoiding the need for thick films. It is likely that the use of conductive diamond would also result in negligible substrate effects. This feature will greatly enhance understanding of the relationships between the intrinsic electrochemical behavior and the electrocatalytic behavior.

2. Experimental details

Microwave plasma-assisted chemical vapor deposition was used to obtain boron-doped polycrystalline diamond films on Si(1 1 1) wafers. The procedure has been described previously [23]. The RuO_2 coatings were prepared by thermal decomposition of an alcoholic solution of $RuCl_3$, at 450 °C in air. Typically, four to six layers of solution were painted on the diamond substrate and each layer was annealed separately. The total amount of deposited oxide (*ca.* 1 mg cm^{-2}) was determined by weighing the samples. All the experiments were performed in a two-compartment cell (7.5 ml catholyte) by using working electrodes of 1 cm^2 area, a platinum counter electrode and a saturated calomel electrode (SCE) as reference.

Cyclic voltammograms were recorded, at room temperature, with a Hokuto Denko HA-502 potentiostat, a Hokuto Denko HB-111 function generator and a Riken Denshi *x*–*y* recorder. Steady-state polarization measurements were carried out under vigorous stirring, by using a Hokuto Denko HA-151 potentiostat. Polarization curves were drawn by applying decreasing potentials in 10 mV steps, and then waiting for 3 min for the current to stabilize. Longtime potentiostatic polarization was also performed for product analysis. After electrolysis, the gas phase was analyzed by gas chromatography (to detect H_2, CO and CH_4) while the solution was checked by gas chromatography and high pressure liquid chromatography (HPLC) for CH_3OH and HCOOH, respectively. The effect of the pH was examined in a series of standard 0.4 M Britton–Robinson solutions (boric acid + phosphoric acid + acetic acid) and the pH was adjusted (within the range 1.8–6.0) by adding appropriate amounts of 1.0 M NaOH solution. In some experiments, a phosphate buffer solution, containing 0.3 M $NaClO_4$, was used. Experiments were performed both in N_2-saturated and CO_2-saturated solutions, at a temperature of 4 °C (if not stated otherwise). All the substances were analytical-reagent grade and all solutions were prepared using Milli-Q water (Millipore).

3. Results and discussion

3.1. *Cyclic voltammetry*

Cyclic voltammograms recorded during 20 consecutive runs (sweep rate 50 mV s^{-1}) in a pH 1.8 Britton–Robinson buffer solution, for RuO_2-coated diamond electrodes (Figure 1) exhibited two broad peaks (labeled I_a and I_c) that are characteristic for RuO_2 voltammetric behavior, mainly in acidic media [29, 30]. The reproducibility of the voltammetric curves indicates the good stability of the electrodes. It is also worth noting that, during several days of experiments, negligible changes of the voltammetric response were observed, which proves the satisfactory adherence of RuO_2 layers at the diamond substrate. Curves from Figure 1 also show that, at RuO_2-coated BDD electrodes, hydrogen evolution is preceded by a cathodic plateau (labeled II), which was not observed for RuO_2–titanium electrodes, either in acidic [20], nor in alkaline media [22]. Elucidating the nature of this plateau is a difficult task and was beyond the scope of the present work. However, preliminary results concerning the effect of the pH and sweep rate seem to indicate that the occurrence of the cathodic

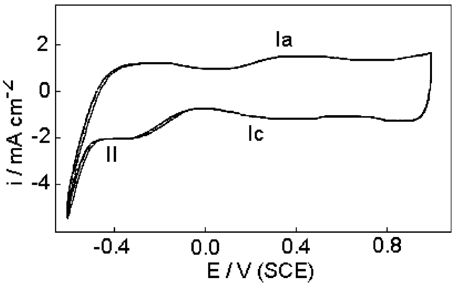

Fig. 1. Cyclic voltammograms recorded at the RuO_2-coated BDD electrodes during twenty consecutive sweeps (scan rate, 50 mV s^{-1}) in Britton–Robinson buffer solution (pH = 1.8).

plateau is strongly related to the proton reduction process. There are reasons to believe that, in the case of RuO_2 deposited on BDD, hydrogen evolution is initially controlled by a mass-transport limited step, probably involving diffusion in the porous structure of the oxide layers. We are currently pursuing this approach in our laboratory and detailed results will be published elsewhere.

In order to assess the electrocatalytic activity of RuO_2 for the reduction of carbon dioxide, cyclic voltammetric measurements were performed both in N_2 and CO_2-saturated solutions. It was found that the results were not very reproducible and subject to interpretation. This is because, during CO_2 bubbling, carbonic acid is formed leading to a change in solution pH. It was observed that usual buffer solutions are often swamped by CO_2 saturation. Figure 2 shows cyclic voltammograms recorded in 0.05 M H_2SO_4 solution (pH 1.5) in the absence (curve 1) and in the presence (curve 2) of dissolved CO_2. Due to the high buffer capacity of the sulfuric acid solution, the pH is not significantly affected by carbon dioxide dissolution, at room temperature. Although the increase in cathodic current is an indication of CO_2 reduction, our experiments suggested that cyclic voltammetry is not a suitable tool for detailed investigation of this process.

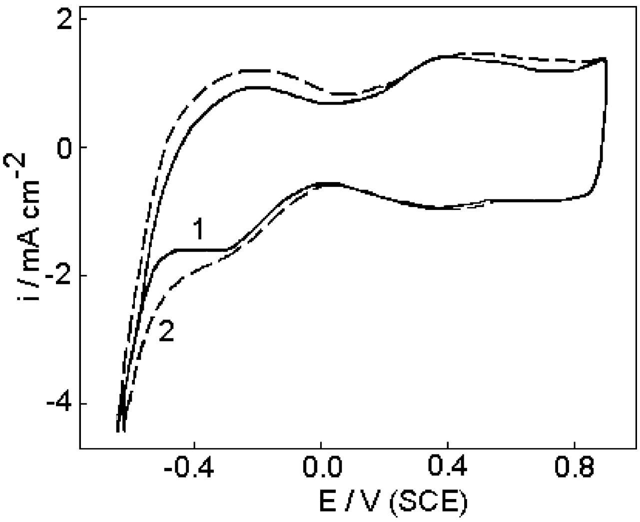

Fig. 2. Cyclic voltammetric response of the RuO_2/BDD electrodes in 0.05 M H_2SO_4 in the absence (1) and in the presence (2) of dissolved CO_2. Sweep rate, 50 mV s^{-1}.

3.2. *Steady-state polarization measurements*

In order to study the influence of the pH on the electrochemical reduction of carbon dioxide at the investigated electrodes, steady-state measurements were performed both in N_2 and CO_2-saturated solutions. A 0.4 M Britton–Robinson solution was used up to pH 6, while at neutral pH the measurements were carried out in a 0.2 M phosphate buffer solution. Within range 2.4–7.5, the extent to which CO_2 dissolution affected the pH was not higher than *ca.* 0.2 pH units. In order to enhance CO_2 solubility, the experiments were performed at a temperature of *ca.* 4 °C. The polarization measurements were carried out under vigorous stirring, in order to minimize the effect of hydrogen coverage. Previously reported data [21] have shown that mass transport does not play a prominent role in the overall process of CO_2 reduction.

Figure 3 summarizes the results of steady-state measurements for several values of pH. It was observed that

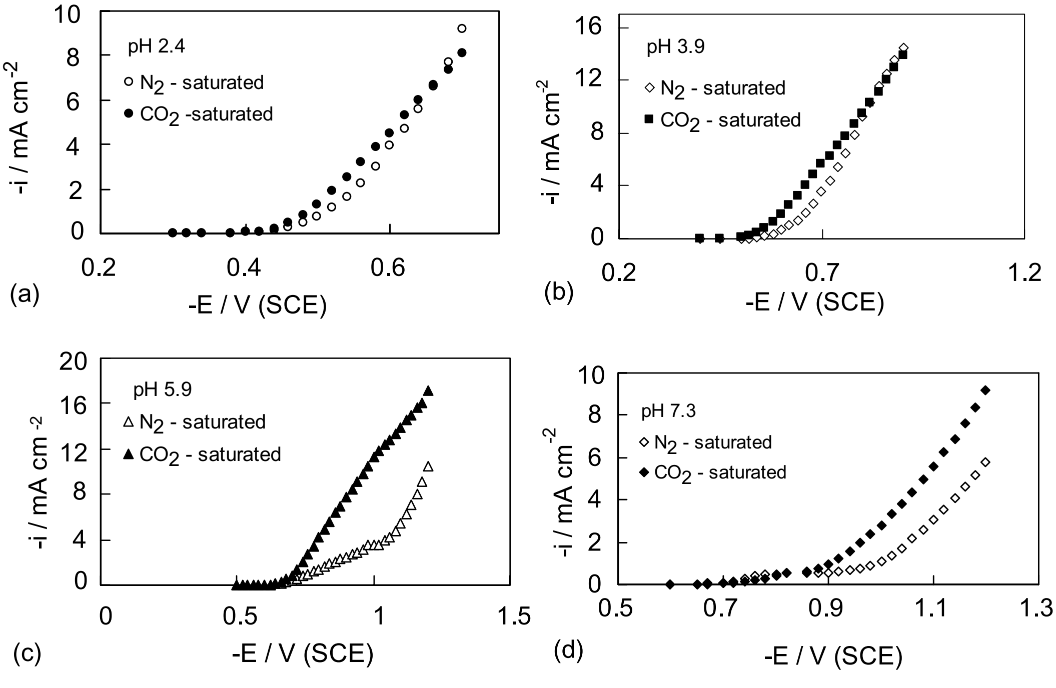

Fig. 3. Steady-state polarization curves in the absence and in the presence of dissolved CO_2 at several values of the pH: (a) pH = 2.4; (b) pH = 3.9; (c) pH = 5.9; (d) pH = 7.3.

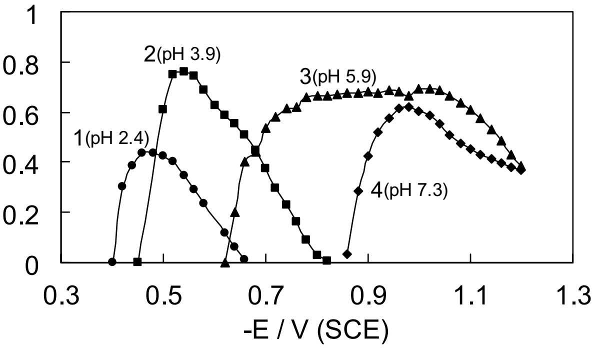

Fig. 4. The ratio of CO_2 reduction current on the total current as a function of the potential at several pH values: (1) pH = 2.4; (2) pH = 3.9; (3) pH = 5.9; (4) pH = 7.3.

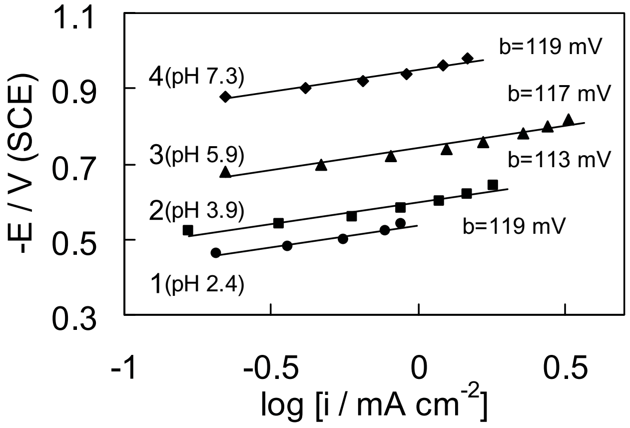

Fig. 5. Tafel plots for CO_2 reduction at the RuO_2-coated BDD electrodes, at several pH values: (1) pH = 2.4; (2) pH = 3.9; (3) pH = 5.9; (4) pH = 7.3.

in the investigated pH range, the reduction of carbon dioxide occurs together with hydrogen evolution. As Figure 3 shows, no significant CO_2 reduction was evident prior to hydrogen evolution onset. Our results suggest that, in acidic media, carbon dioxide reduction is hindered by strong hydrogen discharge (Figure 3a and b) while this is not the case at pH values near neutrality (Figure 3c and d). These findings support the conclusion that higher pH ensures more favorable conditions for the investigated process. Nevertheless, due to the buffer swamping we were not able to investigate the effect of pH above *ca.* 7.5.

Assuming that the increase in current evidenced by the polarization curves is due only to carbon dioxide reduction, the current density for this process (i_{CO_2}) can be estimated as the difference between the current density in the presence (i_t) and absence of dissolved CO_2. Figure 4 shows the variation of the ratio i_{CO_2}/i_t as a function of applied potential for several pH values. These data suggest that, at RuO_2-coated BDD electrodes, the best efficiency for carbon dioxide reduction (almost 80%) could be achieved at pH values around 4.0, for an applied potential of *ca.* −0.55 V (see curve 2 from Figure 4). Although under these experimental conditions i_{CO_2} is rather small, there are reasons to believe that the current density for CO_2 reduction could be significantly improved by running the experiments under high pressure. We are currently pursuing this approach in our laboratory and detailed results will be published elsewhere. It is worth noting that this pH value is close to that of a saturated aqueous solution of carbonic acid (*ca.* 3.7), which could be suitable for practical purposes.

As curve 3 from Figure 4 shows, a pH of *ca.* 6.0 ensures wider potential range for efficient CO_2 reduction. This behavior could allow the galvanostatic control of the electrolysis process, which is more convenient, from a technical point of view, than potentiostatic control. Furthermore, reasonably high current densities for CO_2 reduction are also available, in line with the observation that, at pH values near neutrality, this process is less affected by strong hydrogen evolution.

Tafel plots were also drawn and, as Figure 5 illustrates, the Tafel slopes for various pH values lie between 113 and 119 mV decade^{-1}. Due to the complexity of the CO_2 reduction process, it is likely that these data cannot supply detailed information concerning the reaction mechanism (see Ref. [20] and references therein). Nevertheless, the close values of the Tafel slopes indicate similar reaction paths for carbon dioxide reduction at the RuO_2-coated diamond electrodes within the whole investigated pH range.

3.3. *Longtime polarization measurements*

In order to identify the products obtained by the reduction of carbon dioxide, longtime potentiostatic polarization experiments were performed for several pH values. In each case the pH of the solution was measured while being CO_2 saturated. Electrolysis was performed at a temperature of 4 °C in a two-compartment cell (7.5 ml catholyte) with a working electrode of 1 cm^2 area. For every pH value the applied potential was adjusted to fit within the potential range of the maximum efficiency, as suggested by the data in Figure 4. The gaseous products formed during electrolysis were collected and analyzed by gas chromatography. After electrolysis, the solution from the cathodic compartment of the cell was also analyzed by gas chromatography and HPLC. The current efficiencies were calculated, for each of the identified products, by the following equation:

$$\text{Efficiency}\,(\%) = \frac{Q_{\text{red}}}{Q_{\text{t}}} \times 100$$

where Q_t represents the total % charge corresponding to the electrolysis current, and Q_{red} stands for the charge involved in the reduction of CO_2 to each product, as calculated from the amount of product formed.

Table 1 summarizes the results of longtime polarization experiments performed at RuO_2-coated BDD electrodes in CO_2-saturated solutions, at several pH values. It can be observed that the efficiency for

Table 1. Results of longtime polarization experiments for CO_2 reduction at the RuO_2-coated BDD electrodes, at several pH values

pH	E /V	Total charge /C	Product concentration					Product efficiency /%				
			H_2 /%	CO /ppm	CH_4 /ppm	CH_3OH /ppm	HCOOH /ppm	H_2	CO	CH_4	CH_3OH	HCOOH
2.4	−0.5	50.9	66.07	210.0	196.1	22.17	413.7	59.27	0.02	0.07	5.93	25.18
3.9	−0.6	37.9	26.44	115.9	4625	21.52	496.3	25.25	0.01	1.70	7.73	40.58
5.9	−0.8	51.3	52.70	57.81	375.7	31.31	540.6	39.88	0.005	0.11	8.12	32.66
7.3	−1.0	59.6	64.61	50.75	440.1	20.86	719.6	44.85	0.003	0.12	4.77	37.45

Volume of gaseous products: pH 2.4, 5.3 cm^3; pH 3.9, 4.2 cm^3; pH 5.9, 4.5 cm^3; pH 7.3, 4.8 cm^3.
Polarization time: pH 2.4, 643 min; pH 3.9, 337 min; pH 5.9, 206 min; pH 7.3, 356 min.

hydrogen formation is higher than 50% only at $pH = 2.4$, while at higher pH values CO_2 reduction prevails. The fact that a pH value of *ca.* 3.9 ensures the highest efficiency for the electrochemical reduction of carbon dioxide is also in line with the results of the steady-state measurements, as illustrated in Figure 4. Data from Table 1 show that, within the investigated pH range, the main products of CO_2 reduction are formic acid and methanol. This behavior is in agreement with the close values of the Tafel slopes, indicating similar reaction paths for the electrochemical reduction of the carbon dioxide, both in acidic and neutral media. It was observed that the efficiency for CO_2 reduction, as calculated from the product efficiencies in Table 1, is always lower than would be predicted by the curves from Figure 4. Conversely, in all the cases the efficiency for hydrogen evolution agrees quite well with the results of the steady-state measurements. This could indicate that, besides CO, CH_4, CH_3OH and HCOOH, some other compounds are formed during carbon dioxide reduction. Further experiments are in progress in order to elucidate the actual composition of the electrolysis products, both in the gaseous and liquid phase.

4. Conclusions

Study of carbon dioxide reduction at RuO_2-coated diamond electrodes showed that conductive metallic oxides are promising electrocatalysts for this process and allow higher reduction products to be obtained. The use of BDD as a substrate for the RuO_2 layers resulted in lower Faradaic efficiency for CO_2 reduction to methanol, than reported for the same electrocatalyst on titanium substrate [22]. A possible explanation for this behavior is provided by the fact that the presence of TiO_2 enhances methanol formation [20, 21]. Therefore, it is likely that during thermal deposition of the RuO_2 layers, TiO_2 is also formed due to titanium substrate oxidation. Conversely, it was observed that use of conductive diamond as a substrate for electrocatalysts results in negligible substrate effect. This feature ensures better investigation of the electrocatalytic properties of the conductive metallic oxide and could allow the development of new, effective electrocatalysts.

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References

1. M.M. Halmann and M. Steinberg, ‘Greenhouse Gas Carbon Dioxide Mitigation Science and Technology’ (Lewis Publishers, Boca Raton, 1999).
2. S. Kapusta and N. Hackerman, *J. Electrochem. Soc.* **130** (1983) 607.
3. Y. Hori, K. Kikuchi and S. Suzuki, *Chem. Lett.* (1985) 1695.
4. T. Yamamoto, D.A. Tryk, K. Hashimoto, A. Fujishima and M. Okawa, *J. Electrochem. Soc.* **147** (2000) 3393.
5. K.W. Frese, Jr. and D. Canfield, *J. Electrochem. Soc.* **131** (1984) 2518.
6. K. Ogura and M. Takagi, *Solar Energy* **37** (1986) 41.
7. D.P. Summers, S. Leach and K.W. Frese, Jr., *J. Electroanal. Chem.* **205** (1986) 219.
8. R.L. Cook, R.C. MacDuff and A.F. Sammels, *J. Electrochem. Soc.* **134** (1987) 2375.
9. D.P. Summers and K.W. Frese, Jr., *Langmuir* **4** (1988) 51.
10. S. Kaneco, K. Iiba, N. Hiei, K. Ohta, T. Mizuno and T. Suzuki, *Electrochim. Acta* **44** (1999) 4701.
11. S. Kaneko, K. Iiba, S.K. Suzuki, K. Ohta and T. Mizuno, *J. Phys. Chem. B* **103** (1999) 7456.
12. S. Kaneko, K. Iiba, K. Ohta and T. Mizuno, *Energy Source* **22** (2000) 127.
13. Y. Tomita, S. Teruya, O. Koga and Y. Hori, *J. Electrochem. Soc.* **147** (2000) 4164.
14. A. Kudo, S. Nakagawa, A. Tsuneto and T. Sakata, *J. Electrochem. Soc.* **140** (1993) 1541.
15. K. Hara, A. Tsuneto, A. Kudo and T. Sakata, *J. Electrochem. Soc.* **141** (1994) 2097.
16. T. Saeki, K. Hashimoto, N. Kimura, K. Omata and A. Fujishima, *J. Electroanal. Chem.* **404** (1996) 299.
17. H. De Jesus-Cardona, C. del Moral and C.R. Cabrera, *J. Electroanal. Chem.* **513** (2001) 45.
18. T. Yamamoto, K. Hirota, D.A. Tryk, K. Hashimoto, A. Fujishima and M. Okawa, *Chem. Lett.* (1998) 825.
19. D.A. Tryk, T. Yamamoto, M. Kokubun, K. Hirota, K. Hashimoto, M. Okawa and A. Fujishima, *Appl. Organometal. Chem.* **15** (2001) 113.
20. A. Bandi, *J. Electrochem. Soc.* **137** (1990) 2157.
21. A. Bandi and H.M. Kühne, *J. Electrochem. Soc.* **139** (1992) 1605.
22. J.P. Popic, M.L. Avramov-Ivic and N.B. Vukovic, *J. Electroanal. Chem.* **421** (1997) 105.
23. T. Yano, D.A. Tryk, K. Hashimoto and A. Fujishima, *J. Electrochem. Soc.* **145** (1998) 1870.

24. T.N. Rao, I. Yagi, T. Miwa, D.A. Tryk and A. Fujishima, *Anal. Chem.* **71** (1999) 2506.
25. S. Jolley, M. Koppang, T. Jackson and G.M. Swain, *Anal. Chem.* **69** (1997) 4099.
26. J.C. Angus, H.B. Martin, V. Landau, Y.E. Evstefeeva, B. Miller and N. Vinokur, *New Diamond Frontier Carbon Technol.* **9** (1999) 175.
27. I. Duo, P.A. Michaud, W. Haenni, A. Perret and C. Comninellis, *Electrochem. Solid-State Lett.* **3** (2000) 325.
28. K. Honda, M. Yoshimura, T.N. Rao, D.A. Tryk, A. Fujishima, K. Yasui, Y. Sakamoto, K. Nishio and H. Masuda, *J. Electroanal. Chem.* **514** (2001) 35.
29. S. Trasatti and G. Lodi, *in* S. Trasatti (Ed.), 'Electrodes of Conductive Metallic Oxides, Part A' (Elsevier, Amsterdam, 1980).
30. A. De Battisti, S. Ferro and M. Dal Colle, *J. Phys. Chem. B* **105** (2001) 1679.